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The effect of temperature on the optical absorption edge of thin amorphous oxide films

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The analysis of the optical adsorption edge as a function of temperature is discussed for some thin amorphous films of V_2O_5, Ge/SiO, GeO_2/SiO and V_2O_5/SiO. Experimental measurements in the temperature range 95 to 485 K are discussed in terms of the well-known Urbach rule and the Mott and Davis theory and the respective parameters are estimated. An attempt is made to describe the present data in terms of a possible energy-band diagram.

1. Introduction

The exponential optical absorption edge, the Urbach [1] edge, is a well known feature in the optical properties of crystalline and amorphous semiconductors and insulators. Although there are unresolved theoretical aspects, there is general agreement, for crystalline semiconductors, that the width of the exponential tail is a direct measure of temperature-induced disorder and reflects the thermal occupancy of phonon states in a crystal [2, 3]. This explanation suggests that amorphous semiconductors, in which there is an additional non-thermal component to the disorder, should exhibit a temperature-independent component to the Urbach edge [4–6].

It is furthermore well known that for many glassy and amorphous nonmetallic materials, the optical absorption edge can be divided into two regions. For absorption coefficients $\alpha(\omega)$ of less than $10^4\ \text{cm}^{-1}$ there is usually an Urbach tail where $\alpha(\omega)$ depends on photon energy $\hbar\omega$ as

$$\alpha(\omega) = \alpha_0 \exp(\hbar\omega - \hbar\omega_0)/E_e \qquad (1)$$

where α_0 is a constant, $\omega = 2\pi\nu$ is the angular frequency of the radiation and E_e is often interpreted as the width of the tails of localized states in the gap region. Further up the edges where $\alpha(\omega) > 10^4\ \text{cm}^{-1}$, the absorption takes the form [7, 8],

$$\alpha(\omega)\hbar\omega = B(\hbar\omega - E_{opt})^r \qquad (2)$$

where B is a constant, E_{opt} is the optical energy gap of the material and the exponent r may take values 1, 2, 3, 1/2, 3/2 indicating the type of electron transitions in the k-space. In many amorphous oxides [9–11] the values of E_{opt} decrease almost linearly with increasing values of temperature and can be expressed by the empirical relationship

$$E_{opt} \approx E_{opt}(0) - \gamma T \qquad (3)$$

$E_{opt}(0)$ is a constant and γ is the temperature coefficient of the optical energy gap.

In the following we investigate the temperature variation of the optical absorption edge of amorphous V_2O_5, Ge/SiO, GeO_2/SiO and V_2O_5/SiO thin films. Details of the film preparation and the technique of measuring the temperature effect on the optical absorption have been described earlier [11–13].

2. Results

2.1. Amorphous thin films of vanadium pentoxide

The absorption spectra of amorphous V_2O_5 films of thickness ~ 237 nm at different temperatures are presented in Fig. 1. At a temperature ~ 100° C, the optical absorption edge shifted towards higher wavelengths in a similar way to that of the SiO film [11]. At higher temperatures (~ 200° C), the spectrum shifted towards lower wavelengths. This may be due to a change in the film structure. In

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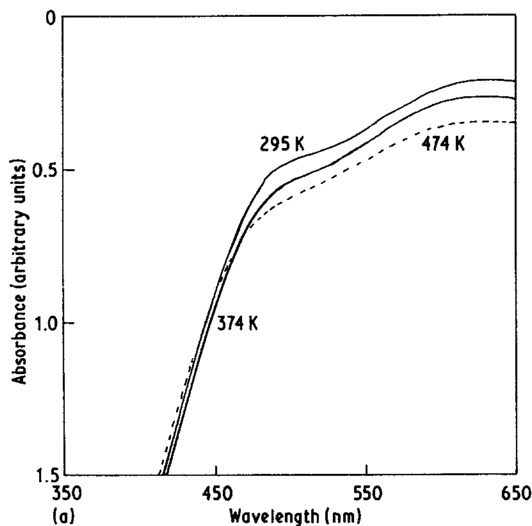

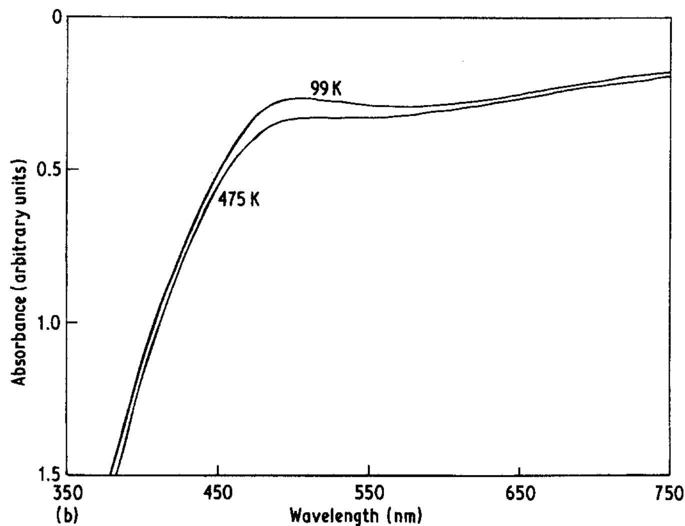

Figure 1 (a) Optical absorbance spectra for a 237 nm thin film of V_2O_5. (b) Optical absorbance spectra for a 140 nm thin film of V_2O_5.

an attempt to clarify the situation, measurements were made on further specimens of thickness ~ 140 nm and the results are also shown in Fig. 1. With the increase of temperature, the optical absorption edge moved slowly towards higher wavelengths. The displacement of the absorption curve was reversible, that is, on returning the sample to room temperature, the original absorption curve was reproduced suggesting that the material had not undergone any permanent structural change.

Fig. 2 shows the exponential edge at different temperatures and the values of the parameter E_e are listed in Table I. For a V_2O_5 single crystal, the value of E_{opt} was found to decrease and E_e to increase linearly with temperature in the range 293 to 653 K. Amorphous V_2O_5 films are known [15] to fit Equation 2 with $r = 3/2$. The variation of E_{opt} with temperature (Fig. 3) is small and the γ-value is found to be $- 1.6 \times 10^{-4}$ eV K^{-1}.

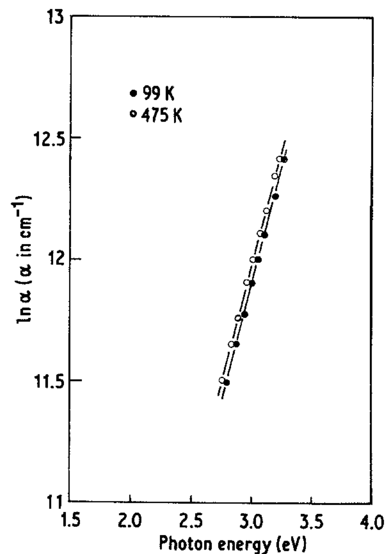

Figure 2 Absorption coefficient as a function of photon energy for the V_2O_5 film of Fig. 1b.

TABLE I Some optical parameters of amorphous thin oxide films at different temperatures

Amorphous sample	Temperature (K)	E_{opt} (eV)	E_e (eV)	B (cm^{-1} eV^{-1})
V_2O_5	99	2.52	0.53	–
	474	2.46	0.53	–
Ge/SiO	93	2.31	0.47	2.50×10^5
	295	2.25	0.47	2.50×10^5
	480	2.20	0.46	2.50×10^5
GeO_2/SiO	96	2.05	0.61	1.60×10^5
	295	1.92	0.64	1.60×10^5
	486	1.87	0.64	1.60×10^5
V_2O_5/SiO	98	2.55	1.40	0.54×10^5
	480	2.45	1.40	0.54×10^5

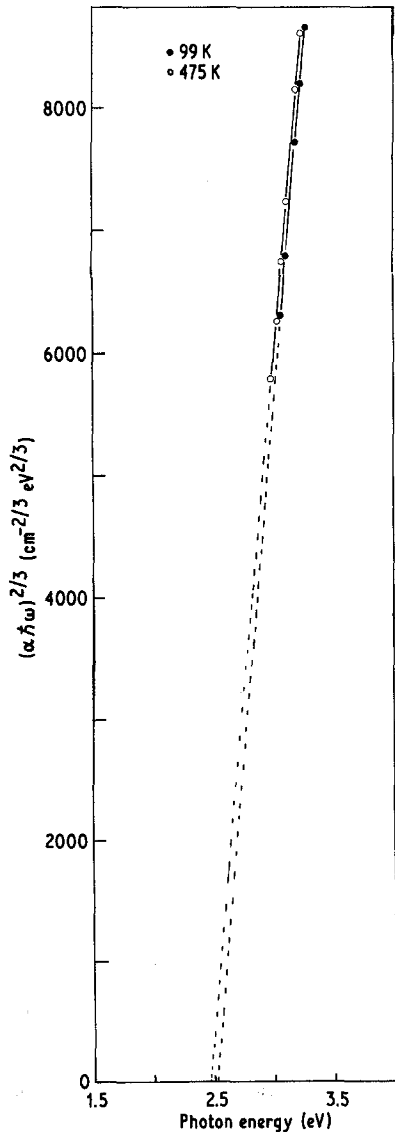

Figure 3 $(\alpha\hbar\omega)^{2/3}$ as a function of photon energy for the V_2O_5 film of Fig. 1(b).

2.2. Amorphous thin films of the Ge/SiO system

Plots of $(\alpha\hbar\omega)^{1/2}$ as a function of photon energy for an amorphous Ge/SiO film of thickness ~ 655 nm at three temperatures are shown in Fig. 4. The values of E_{opt} and the constant B are obtained and listed in Table I. The value of γ is found to be -2.84×10^{-4} eV K^{-1}. Fig. 5 shows the variation of the absorption spectra with temperature in the Urbach tail region. From the slope of the exponential edge, the values of E_e are listed in Table I. The refractive index, n_f, estimated from the interference fringes [16] in the visible region is shown in Fig. 6 to decrease with increasing temperature.

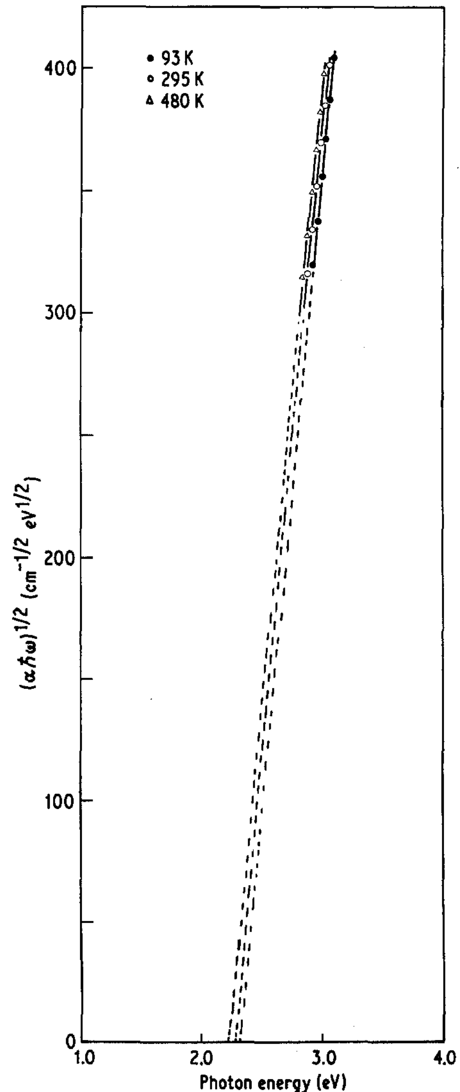

Figure 4 Dependence of $(\alpha\hbar\omega)^{1/2}$ on photon energy for a Ge/SiO thin film at three temperatures.

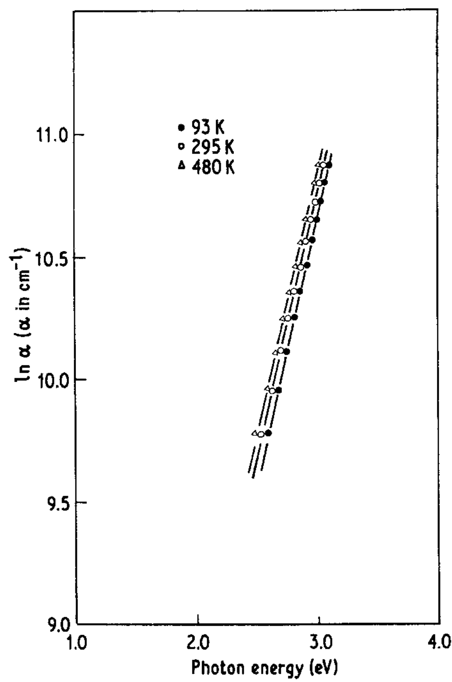

Figure 5 Absorption coefficient as a function of photon energy for a thin Ge/SiO film at three temperatures.

2.3. Amorphous thin films of the GeO_2/SiO system

The exponential dependence of α on $\hbar\omega$ for an amorphous GeO_2/SiO film (thickness ~ 474 nm) is shown in Fig. 7 and values of E_e are calculated and listed in Table I. The optical data are fitted outside the exponential region by the expression $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$ as shown in Fig. 8 and the respective values of E_{opt} and B are listed in Table I. The γ-value appears to be -4.63×10^{-4} eV K^{-1}. The estimated value of n_f is found to be ~ 2.3 and is almost independent of the temperature.

2.4. Amorphous thin films of the V_2O_5/SiO system

The analysis of the high absorption region of amorphous V_2O_5/SiO thin films has been presented on the basis of a chemical interaction between the two oxides [15]. We are only concerned here with the temperature dependence of the absorption edge and in order to extract the necessary parameters we shall analyse the results assuming non-direct optical transitions, i.e. $r = 2$. The parameter $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$ for an amorphous V_2O_5/SiO film (thickness ~ 485 nm) is shown in Fig. 9 and the respective values of E_{opt} and B are listed in Table I. The γ-value is found to be -2.62×10^{-4} eV K^{-1}. From the Urbach plot, Fig. 10, the values of E_e are estimated and are also included in Table I.

3. Discussion and conclusion

It is well known that in many crystalline insulators [17, 18], there is a displacement of the absorption edge towards longer wavelengths with increasing temperatures. This is manifested in many cases by a deepening of the colour. It is noted from the novel data presented above that the absorption edge broadens and shifts to lower energy with increasing thermal disorder. The constant B is found to be temperature independent similar to that for amorphous $Si(H_x)$ films [19]. Cody *et al.* found linear relationships between $E_{opt}(T)$ and $E_e(T)$ in amorphous $Si(H_x)$ films confirming that their temperature dependence has the same functional form. For the V_2O_5, Ge/SiO, GeO_2/SiO and V_2O_5/SiO films, however, the value of E_e is considered to be essentially independent of temperature in qualitative agreement with results for amorphous WO_3 and for As_2O_5/SiO thin films [10, 20].

Varshani [21] showed that with the increase of temperature, the absorption edge energy decreases

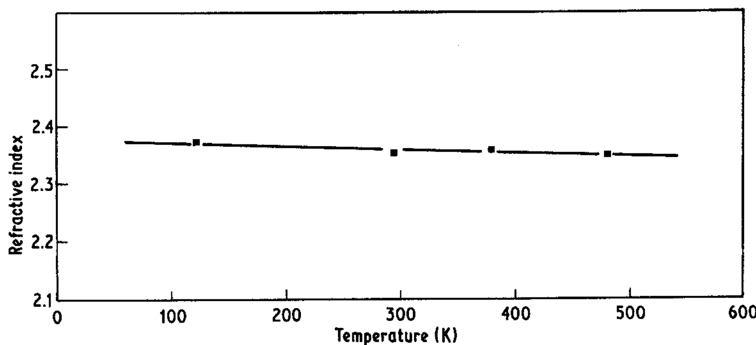

Figure 6 Variation of refractive index of a thin Ge/SiO film with temperature.

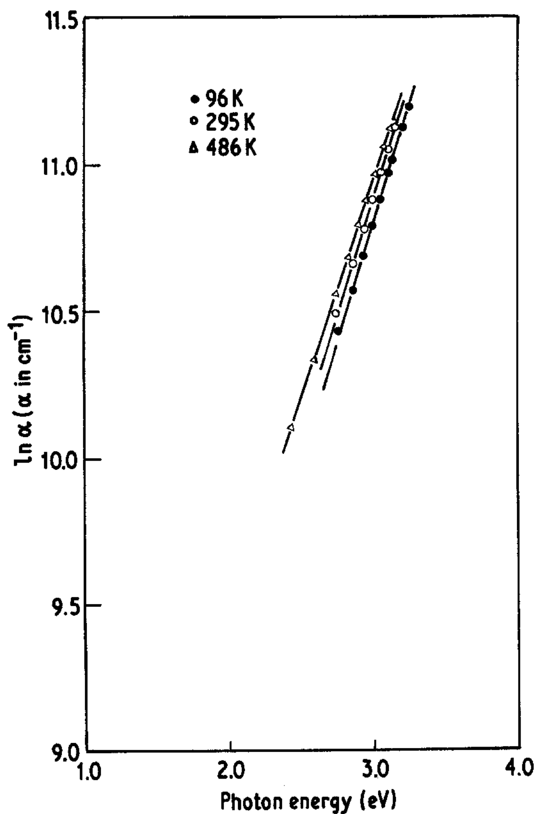

Figure 7 Absorption coefficient as a function of photon energy for a thin GeO_2/SiO film at three temperatures.

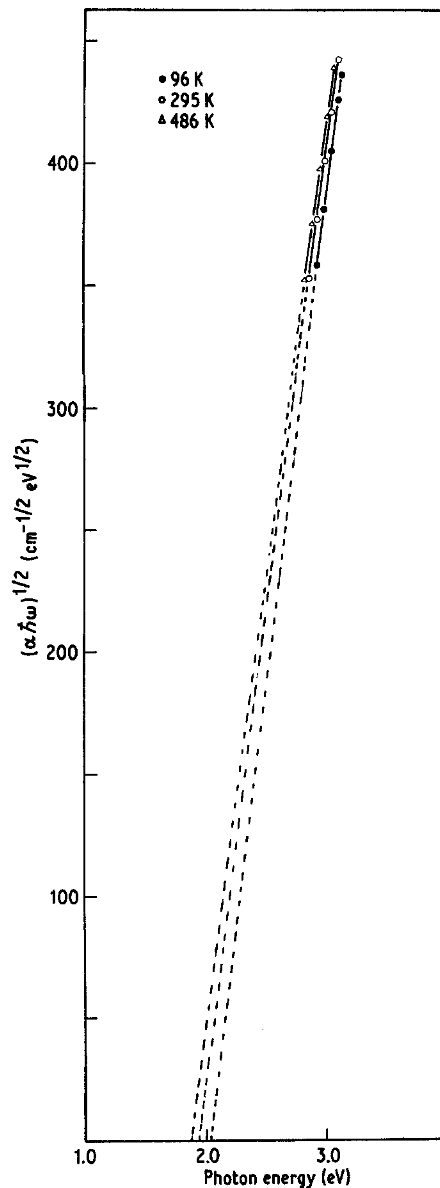

Figure 8 Dependence of $(\alpha\hbar\omega)^{1/2}$ on photon energy for a GeO_2/SiO thin film at three temperatures.

and hence the band gap decreases. This suggests that with the increase of temperature the absorption edge should shift towards longer wavelengths in amorphous semiconductors, due to the similarity in the broader feature (i.e. the short-range order) of crystalline and amorphous materials. Our results clearly show the dependence of the absorption edge on temperature and, in accordance with Varshani's formulation, the shift of the absorption edge is towards longer wavelengths as the temperature increases.

In most amorphous oxides, the linear dependence of the optical band gap with temperature is obtained with a negative temperature coefficient of the same order as reported earlier in the literature [9, 10, 20].

Generally only a few reports on the temperature effect on the refractive index were found [22]. For example, amorphous silicon [23], SiO [11] and tin disulphide [24] thin films are reported to have lower values of n_f with increasing temperature in qualitative agreement with this work.

The results may be understood, at least qualitatively, with reference to the type of density-of-states functions for these amorphous materials [11, 20] as shown in Fig. 11. The mobility gap and the optical energy gap are both related to the point of inflection in the curve of $N(E)$ against E, the electron energy, which determines when band tailing into localized states becomes significant. With varying temperature in these amorphous films leading to increased thermal disorder, the band tailing starts at lower energies but remains invariant into the forbidden gap as shown by the band tails in Fig. 11. Hence the value of E_{opt} is

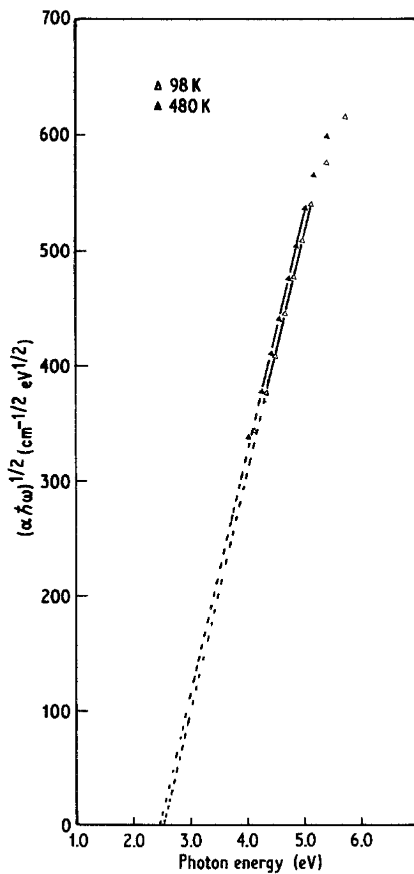

Figure 9 Dependence of $(\alpha\hbar\omega)^{1/2}$ on photon energy for a V_2O_5/SiO thin film at two temperatures.

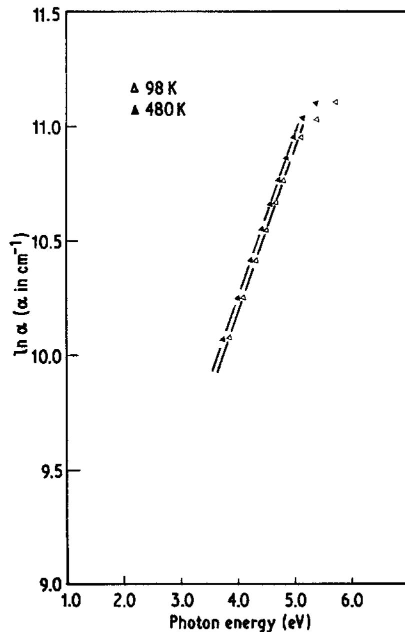

Figure 10 Absorption coefficient as a function of photon energy for a thin V_2O_5/SiO film at two temperatures.

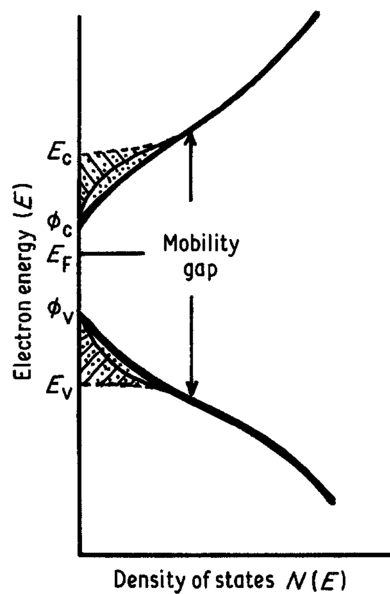

Figure 11 Density-of-states diagram for amorphous oxide thin films. E_c, E_V represent band edges of possible crystalline material; E_f is Fermi energy; ϕ_c, ϕ_V represent the extent of band tailing. The band curvature between the mobility shoulder and ϕ_c or ϕ_V depends on the temperature.

expected to reduce but E_e will remain almost invariant with temperature.

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